

The University of Chicago

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A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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A $^1\Sigma \rightarrow ^1\Sigma$ Transition of the C_2 Molecule

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The $\lambda 2300$ "band" of the carbon arc, previously noticed by Bloomenthal and other investigators and measured by Hori, who attributed it to a C_3 molecule, has been accurately measured and analyzed, using photographs taken on the 30-foot, 30,000-line grating spectrograph. The analysis shows definitely that the structure consists of superposed (0,0), (1,1), (2,2), and (3,3) headless bands of a $\Sigma \rightarrow \Sigma$ transition of C_2 (or possibly C_2^+), in agreement with the earlier diagnosis of Mulliken and Dieke. Alternate lines are missing in each series, as expected in view of the zero spin of the carbon nucleus. Most probably the

transition is $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ of C_2 . The molecular constants are very nearly equal for the upper and lower electronic states. They correspond rather closely to the average values of the same constants for other known states of C_2 . The following values were obtained for the more important constants: $B_e' = 1.8334 \text{ cm}^{-1}$, $B_e'' = 1.8223 \text{ cm}^{-1}$, $\alpha' = 0.0204$, $\alpha'' = 0.0195$, $r_e' = 1.2382 \text{ \AA}$, $r_e'' = 1.2419 \text{ \AA}$, $\omega_e' = 1748 \text{ cm}^{-1}$, $\omega_e'' = 1774 \text{ cm}^{-1}$, $\nu_0^{0,0} = 43,227.25 \text{ cm}^{-1}$. The ω_e values were obtained indirectly from the B and D values, since only one sequence of bands could be analyzed.

INTRODUCTION

BECAUSE of its importance in the study of molecular structure in general and in particular in the study of problems that arise in

organic chemistry, the electronic transitions of the diatomic carbon molecule and the determination of related constants have been of considerable interest to the physicist and the

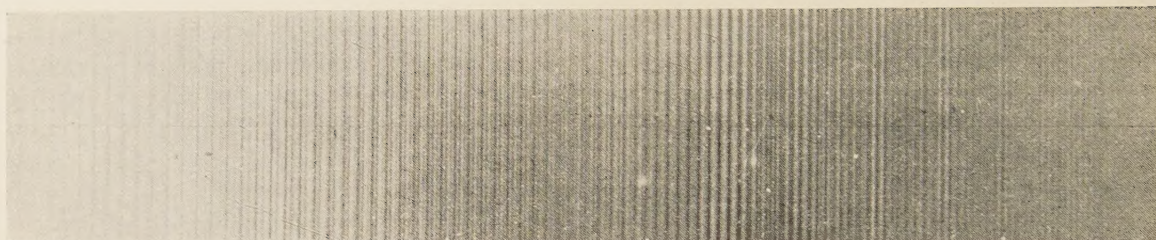


FIG. 1. The band at $\lambda 2300\text{\AA}$ reproduced from a picture that was taken with a Hilger E 1 spectrograph by Dr. S. Bloomenthal.

chemist alike. The subject of the present work is the analysis of a band which apparently occurs regularly in the spectrum of the carbon arc near $\lambda 2300\text{\AA}$. So far as the writer is aware, the first published mention of this band is in an article by Mulliken¹ in 1930. The band was discovered in this laboratory by Dr. S. Bloomenthal in 1928–29, by using a carbon arc in hydrogen at low pressure in a search for boron hydride bands. It was also discovered independently by Professor G. H. Dieke. Later it was reported and measured by Hori.² It has also been reported by G. and L. Herzberg,³ who state that they have made a partial analysis. Very likely the band has been noticed independently also by others.

Both Mulliken and Dieke interpreted the "band" as the $\Delta v=0$ sequence of a $^1\Sigma \rightarrow ^1\Sigma$ transition of the C_2 molecule. However, attempts to confirm this view by rotational analysis have hitherto not been carried through. Dr. S. Bloomenthal and also S. D. Ginsberg did a considerable amount of work on the band in this laboratory but did not have sufficient dispersion and resolving power to accomplish a satisfactory analysis. Fig. 1 is a reproduction of one of Dr. Bloomenthal's pictures, which he has very kindly supplied. It was taken with a Hilger E 1 spectrograph.

As can be seen from Fig. 1, the $\lambda 2300$ band has all the earmarks of a $\Delta v=0$ sequence of a transition with nearly zero change in moment of inertia and $\Delta\Lambda=0$.⁴ The structure has a central minimum and a maximum on each side with no obvious heads. There are no other obvious bands of comparable intensity in the neighborhood which would correspond to $\Delta v=1$ or further

sequences. This is what one expects if there is very little change in moment of inertia between upper and lower electronic states. The complex appearance of the band (presence of several series) is what would be expected if several members of the $\Delta v=0$ sequence are present. The fact that the bands usually appear with known C_2 bands, and the spacings of the lines in series indicating a B value about right for a C_2 molecule, provided alternate lines are missing in each series as required for a $^1\Sigma \rightarrow ^1\Sigma$ transition in C_2 , made the latter very probable. The present analysis bears out this diagnosis. Three bands identified as (0,0), (1,1), and (2,2) have been completely analyzed. The strongest portions of the (3,3) band have been measured.

There has existed hitherto only one published attempt at the analysis of these bands. This is in the paper by Hori referred to above. The strongest lines were arranged in a single series with no missing line at the center. Hori concluded from this last circumstance that the band cannot be due to a diatomic $^1\Sigma \rightarrow ^1\Sigma$ transition and tentatively ascribed it to a C_3 molecule.

Hori's strongest series and the writer's (0,0) band are identical except across the central minimum. Here Hori uses the range from $R(12)$ to $R(28)$ of the writer's (3,3) band in place of lines $P(8)$ to $R(8)$ of the (0,0) band. It happens that $R(12)$ and $R(28)$ of the (3,3) band are not resolved from $P(8)$ and $R(8)$, respectively, of the (0,0) band. In this manner, Hori constructed an apparent series in which the intensities did not approach zero in the central region and in which no line was missing. When, however, a study was made of Hori's series, using the writer's more accurate measurements, it was found that at the two points at which Hori switched from one series to another, a sudden

¹ R. S. Mulliken, *Zeits. f. Electrochemie* **36**, 603 (1930).

² Takeo Hori, *Zeits. f. Physik* **88**, 495 (1934).

³ J. G. Fox and G. Herzberg, *Phys. Rev.* **52**, 638 (1937).

⁴ Cf. R. S. Mulliken, *Rev. Mod. Phys.* **3**, 149 (1931).

break occurred in the first differences. It was found possible, by departing from Hori's arrangement, to extend the series in such a way that the first differences progressed perfectly smoothly past these points. In this way, the true series comprising the (0,0) band was found.

EXPERIMENTAL PROCEDURE

In all previous work on the $\lambda 2300$ band the source has been an enclosed carbon arc. This was made necessary by the fact that, while the bands are produced at least as rapidly in air as in other gases, they are then overlain by bands of impurities, particularly CO bands. The CN bands are, of course, also strong, but do not extend to $\lambda 2300$. Hori² used a metal cylinder for enclosing the arc. Bloomenthal in his work here used a Pyrex bulb. In both cases the graphite electrodes were placed so that their axes were in a straight line and the gap was adjusted by screws which extended to the outside of the bulb. Both experimenters ran the arc in hydrogen at pressures ranging from 8 to 50 cm of mercury. It was possible to use hydrogen since no CH bands appear in the $\lambda 2300$ region.

In the present work the source was a carbon arc with the electrodes at right angles, enclosed in a five-liter Pyrex bulb. The apparatus was of conventional design except that air leakage was prevented by using sylphons fitted over bent rods the rotation of which operated the screw mechanism of the water-cooled electrodes.

Helium was found to be a suitable gas in which to operate the arc. In the first place, helium eliminates the danger of explosion. Further, the only spectrum produced by helium in the carbon arc is its line spectrum, which does not fall in the $\lambda 2300\text{\AA}$ region. Finally, it was found that sufficient purity of the gas could be obtained by merely confining tank helium for some time in a charcoal liquid air trap.

The pressure of helium was found not to be critical. The $\lambda 2300$ band occurs at all pressures from 0.1 mm of mercury or less to atmospheric pressure. Using solid electrodes, a pressure of about 6 cm was found to give the best results. When hollow electrodes were used (see description below), the range from 0.5 to 2.0 cm of mercury produced a somewhat higher intensity with less background than other pressures. This

pressure range was actually used for the final exposures.

In view of the close spacing and many blends indicated by the work of previous investigators, it was obvious that a matter of first importance was to increase the accuracy of measurement and the degree of resolution of the lines of the spectrum. It appeared that the high resolving power and especially the high dispersion of the laboratory's 30-foot, 30,000-line/inch grating spectrometer would be suitable for the purpose. Now the 30-foot spectrometer requires a very much longer time of exposure than the smaller instruments. Furthermore, the length of exposure which can be used is limited by the fact that, with full resolving power, only a minor change in barometric pressure is allowed. It, therefore, was necessary to have a light source of high intensity so that the time of exposure might be kept sufficiently short.

It was found that when solid graphite electrodes were used, enough intensity could not be attained. However, when $\frac{5}{32}$ " holes were drilled into the $\frac{3}{8}$ " electrodes, the cathode end of the arc, which wandered badly when solid electrodes were used, then settled into the cavity. When the arc was right-angled and the hollow cathode was placed facing toward the slit, not only did this produce a steady source of ideal dimensions for use with the 30-foot spectrograph, but also the heating effect was more concentrated and diffusion was retarded so that relatively more carbon vapor was available for the production of C_2 molecules. Also, the sputtering which takes place from a solid cathode and which consumes the cathode at a rate of about $\frac{1}{8}$ inch/hour was completely stopped. It is estimated that this change increased the intensity of the band at $\lambda 2300\text{\AA}$ by a factor of fifty or more, using a current of 20 amperes at 220 volts. It was found possible to produce a further increase in intensity of perhaps six times by raising the current to 30 amperes, but this was not necessary.

As previously mentioned, the 30-foot, 30,000-lines/inch grating spectrograph was used. The grating was ruled on speculum metal in this laboratory by Dean Henry G. Gale, and afterwards was given a thin coat of aluminum by evaporation, in order to increase its ultraviolet reflecting power. The grating is set up in Paschen

mounting and has six inches of ruled surface. The grating shows excellent resolving power. In the fourth order a resolving power of at least 420,000 has been observed by Dr. Beutler in an examination of mercury hyperfine structure.

The grating is so ruled that its maximum intensity for $\lambda 2300$ is in the third order. This fact combined with the very favorable dispersion made it desirable to use the third order. It is then necessary to remove the second order of $\lambda 3450\text{\AA}$, since under certain operating conditions the Swan bands of C_2 appeared strongly in this region, as also a certain amount of continuous light from the arc. For this purpose a quartz chlorine filter was used. An effective length equivalent to 1 cm of chlorine gas at atmospheric pressure was found to be suitable.

In the third order of $\lambda 2300\text{\AA}$, the dispersion is about $0.25\text{\AA}/\text{mm}$. Now the temperature of the carbon arc source of the $\lambda 2300$ band is estimated to be at least 3500°C . If the emitter is assumed to be C_2 , the Doppler width of the band lines from this source is calculated to be $0.02\text{\AA}$ (0.08 mm on the third-order plate). Therefore, a slit width of 0.04 mm ($=\frac{1}{2}$ Doppler width) is permitted because it reduces the resolution by only 10 percent. This gives an actual resolving power of about 60,000 in third order. This is much less than the grating could give but the high dispersion was very desirable. The slit width used in the present work was 0.04 mm , except in one case in which the width of 0.025 mm was used. As was expected, the smaller slit width merely increased the time required for exposure without increasing the resolution.

Three good exposures were made of two, five, and nine hours duration, and with respective slit widths of 0.04 , 0.04 , and 0.025 mm . The length of exposure was limited by continuous light which tended to mask the weakest lines. The exposures were made on Eastman type I-O plates, ultraviolet sensitized.⁵

The discharge of the carbon arc in helium when hollow electrodes, such as are described above, are used, exhibits certain interesting

properties. If we assume, as is quite probable, that the lower $^3\Pi$ state of the Swan bands, which is thought to be the normal state, and the lower $^1\Sigma$ state of the $\lambda 2300$ bands lie close together, the higher frequency of the $\lambda 2300$ band indicates that the energy required to excite it must be greater than for the Swan bands. We would, therefore, expect the Swan bands to be produced strongly whenever the $\lambda 2300$ bands appear. When, however, the hollow cathode carbon arc is used, the Swan bands disappear. The spectrum then consists only of the $\lambda 2300$ bands, a few lines due to impurities in the electrodes, and the helium spectrum. This seems very strange, yet there can be no doubt that the $\lambda 2300$ bands are produced by C_2 , as is shown by the present analysis. (The possibility of C_2^+ is not thereby excluded.)

The fact that the helium spectrum appears strongly shows that electrons with energy approaching 25 volts are present in the discharge. The general appearance of the arc also suggests that the discharge is largely electronic.

EXPERIMENTAL DATA

Below are presented the data on which the detailed analysis is based. Table I is a list of the measured values of the observed lines in cm^{-1} in vacuum. The probable errors of measurement, except for a few very weak lines, are well within $\pm 0.2\text{ cm}^{-1}$ (or $0.01\text{\AA}$). Fully one-third of the lines, however, are blends. A major fraction of these are near the origins of the bands where intensities are low. There may be errors up to $\pm 1.0\text{ cm}^{-1}$ when such lines are fitted into series. The intensities, as estimated from the heights of peaks in microphotometer traces, are indicated in the column marked *I*. The columns that contain the J'' assignments are labelled 0, 1, 2, 3 for the (0,0), (1,1), (2,2), and (3,3) bands, respectively.

THEORY AND ANALYSIS OF THE BAND STRUCTURE

As is well known, $^1\Sigma \rightarrow ^1\Sigma$ transitions have simple *P* and *R* branches and no *Q* branch. When the molecule consists of two like atoms, the rotational states are classified as positive and negative as usual, but also as symmetrical and antisymmetrical (*s*, *a*). Transitions can occur

⁵ These plates are decidedly grainy. They were, however, roughly five times as sensitive in the $\lambda 2300$ region as Process or Eastman 33 plates. The Eastman Company states that they are as sensitive as Schumann plates down to $1800\text{\AA}$. They are much more convenient to use.

TABLE I. Wave numbers and identification of band lines of $C_2 \lambda 2313$. Numbers under the headings 0, 1, 2, 3 (each heading denotes $v' = v''$) are J'' for the lines. Intensities I are estimated from microphotometer traces.

$\nu(\text{VAC})$	I	0	1	2	$\nu(\text{VAC})$	I	0	1	2	$\nu(\text{VAC})$	I	0	1	2	3	$\nu(\text{VAC})$	I	0	1	2
43,026.8	0				43,140.4	4		18		43,230.9	0	0		14		43,322.3	1		30	
37.3	0				41.2	6	26		10	34.2	2			8		25.0	5	24		
45.4	2				47.1	7	24	16		36.8	3				22	27.5	1			38
50.5	2	62		40	48.2	0			8	37.9	1					30.5	2			32
54.5	4	60		38	53.0	6	22	14		38.3	2	2				33.4	5	26		
56.4	2				55.0	00			6	38.8	0			16		35.8	1			40
58.6	2	58			56.0	0				42.3	3		10			39.0	2			34
60.3	0		46	36	59.5	6	20	12		44.5	2			24		41.6	5	28		
62.9	3	56			61.5	00			4	45.7	3	4				44.3	0			42
65.5	0		44		65.7	6	18			46.8	2			18		49.4	1			36
67.3	2	54		34	66.4	1		10		50.1	2		12			50.1	5	30		
69.1	1				68.8	000			2	52.4	2			26		52.4	0			44
70.5	1		42		72.2	5	16			53.3	4	6				55.8	1			38
72.2	1	52			73.5	1		8		54.7	2			20		58.6	6	32		
72.7	2			32	76.5	00			6	57.6	3		14			60.9	00			46
76.1	2		40		78.8	5	14			60.3	3			28		64.5	1			40
76.8	3	50			80.2	1		6	0	60.7	5	8				67.4	4	34		
78.4	3			30	83.2	000			8	62.5	2			22		69.3	0			48
81.5	5	48	38		85.3	5	12			65.6	3		16			72.8	1			42
84.4	3			28	86.8	00		4	2	68.5	6	10		30		75.8	3	36		
86.7	5	46	36		90.1	000				70.4	10			24		77.5	1			50
90.6	3			26	92.0	4	10			72.0	10					81.6	0			44
91.6	4	44			93.8	00		2	4	73.4	3		18			84.6	3	38		
92.3	4		34		95.8	000				75.6	1					86.1	0			52
96.7	4	42		24	98.9	3	8		12	76.3	6	12		32		90.2	0			46
97.8	3		32		43,200.9	0			6	78.3	2			26		93.3	2	40		
43,102.1	3	40		22	03.3	000				81.4	3		20			98.7	0			48
03.7	2		30		05.8	3	6	0	14	84.4	6	14				43,402.0	2	42		
07.3	3	38			08.6	0			8	86.6	2			28		02.9	0			
08.7	1			20	10.0	0				89.5	3		22			07.1	2			50
09.7	4		28		12.8	2	4	2		92.4	6	16				11.1	1	44		
12.7	4	36			13.5	0			16	94.7	1			30		15.7	1			52
15.5	4		26	18	14.8	1				97.4	3		24			19.8	2	46		
18.2	5	34			16.3	0			10	43,300.3	6	18				24.4	0			54
21.6	5		24	16	16.9	1				02.8	2			32		28.6	1	48		
23.6	5	32			18.2	0				05.8	3		26			37.6	1	50		
27.7	5		22	14	19.8	1	2	4		08.4	5	20				46.4	1	52		
29.4	5	30			21.3	1			18	11.1	1			34		55.3	1	54		
34.0	4		20	12	23.6	0			12	13.9	2		28			64.1	0	56		
35.4	5	28			27.0	1		6		16.7	5	22				73.2	1	58		
38.1	0				28.9	3			20	19.2	1			36						

only $+\leftrightarrow -$ and $s \leftrightarrow s$ or $a \leftrightarrow a$. If the nuclear spin is zero, as is true for the carbon atom, only the symmetrical states exist. Under these conditions $^1\Sigma \rightarrow ^1\Sigma$ transitions produce bands which have only lines with even J'' for $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ and J'' odd for $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$.^{4, 6, 7} The predicted structures for the case $B' = B''$ are shown in Fig. 2. The intensities of the lines near ν_0 , where the Boltzmann factor may be disregarded, are given by

⁶ $^1\Sigma^+ \leftrightarrow ^1\Sigma^-$ is theoretically impossible. $^1\Sigma_g^- \rightarrow ^1\Sigma_u^-$ produces the same rotational structure as $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ so that these two types cannot be distinguished by rotational analysis. $^1\Sigma^- \rightarrow ^1\Sigma^-$ transitions are rare, however. Furthermore, if it is close to the normal state, as is probable here, the lower $^1\Sigma$ state is expected from configuration theory to be $^1\Sigma_g^+$. For a complete discussion of the possible states of C_2 , see the accompanying article by R. S. Mulliken in this issue of the Review.

⁷ Cf. R. S. Mulliken, Rev. Mod. Phys. 4, 66 (1932).

the simple expression $I \propto (J' + J'' + 1)$.⁸ This gives nearly equal intensity for the P and R branches.

In the present analysis of the $\lambda 2300$ band, the first step was to arrange the lines in series, beginning with a strong series. This was facili-

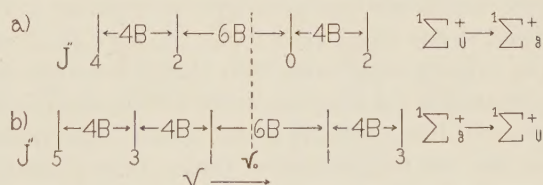
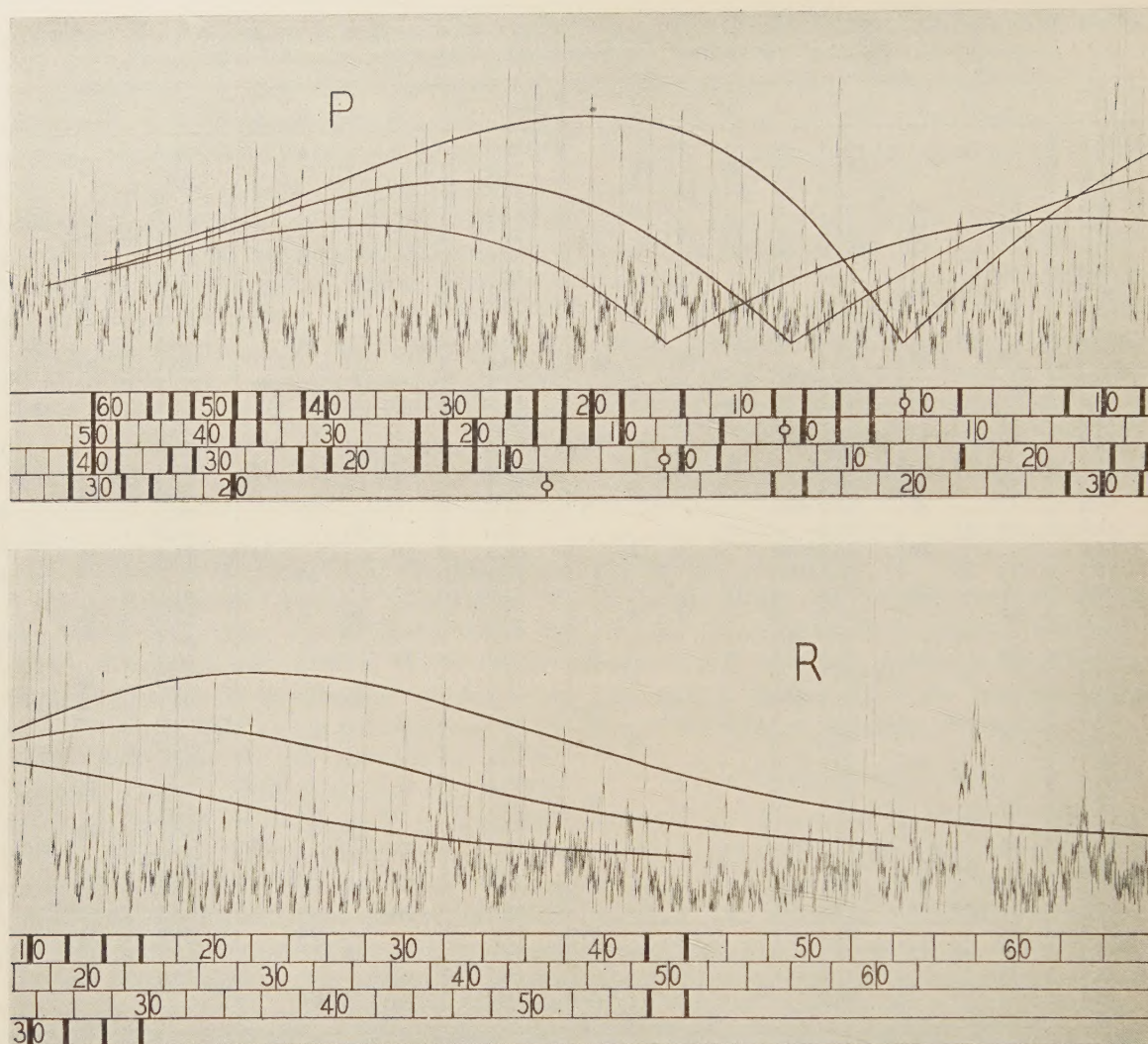


FIG. 2. Predicted structures for $^1\Sigma^+ \rightarrow ^1\Sigma^+$ bands in C_2 for $B' = B''$.

⁸ Cf. W. Jevens, A Report on the Band Spectra of Diatomic Molecules (London: The Physical Society, 1932), p. 134.



FIGS. 3a AND 3b. Microphotometer trace of the $\lambda 2300$ band. The smooth curves are intensity curves drawn in each individual band through the peaks of the unblended lines. The diagram represents the lines of each individual band, with their J'' numbers. The heavy bars of the diagram indicate blended lines.

tated in the case of the (0,0) band by the use of a microphotometer trace of the band. Figs. 3a and 3b constitute a reproduction of such a trace; the lines are shown analyzed into four series attributed to the four bands (0,0), (1,1), (2,2), (3,3). The lines of each band with their J'' values are indicated in the diagram below the figure. It will be noted that there are many blends. Superposed on the microphotometer trace, three smooth intensity curves have been drawn, one for each of the three strongest bands. The curves are drawn through the peaks of those lines in each band that are not blended.

It is seen that a strong R branch and a strong P branch are joined to form what is interpreted as the (0,0) band. This band conforms to one of the $^1\Sigma \rightarrow ^1\Sigma$ types discussed above. The lines are nearly uniformly spaced on both sides of a central intensity minimum, but at this point there occurs a gap which has just $\frac{3}{2}$ times the normal spacing. On the basis of intensities the position of this gap seems to be uniquely determined. In this space, to be sure, there are four weak lines, but these can be attributed to other bands.

We still have a choice of two positions for ν_0 of

the strongest band, each approximately occupied, as it happens, by a line of another band. This choice depends on whether we assume case *a* or case *b* of Fig. 2. If we assume case *a*, then ν_0 must be located as shown in the diagram of Fig. 3. This would require that intensities increase in the order $R(0)$, $P(2)$, $R(2)$, $P(4)$, and so on, proportionately to $J' + J'' + 1 = 2, 4, 6, 8$, and so on. If we take account of the disturbances due to blended lines, it is seen that the intensities as judged from Fig. 3 agree well with the above ratios. This choice for ν_0 makes the transition $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ (case *a*), which is the transition that seems most probable from configuration theory. It will, therefore, be assumed in the following analysis that the bands are of this type.

It should, however, be pointed out that the alternative choice of ν_0 (case *b*, $^1\Sigma_g^+ \rightarrow \Sigma_u^+$) is not entirely incompatible with the observed intensities, in view of the numerous blends. Case *b* would give slightly different values of the rotational constants. Theoretically a choice between the two cases could be made from a study of the $\Delta_2 F$'s. Unfortunately, however, this would demand measurements of an accuracy which is not here realized and probably cannot be.

The ν_0 's of the (1,1) and (2,2) bands were located in relation to $\nu_0^{0,0}$ by a study of first differences between successive lines in the bands. From Fig. 2 it is seen that these differences are all $4B$ if every other line is missing and $B' = B''$. When $B' > B''$, as is the case in the $\lambda 2300$ bands, the first differences are greater than $4B''$ in the *R* branch, less than $4B''$ in the *P* branch and nearly exactly $4B''$ at ν_0 . Now for the *B*'s of bands in a sequence we may assume the usual relation $B_v = B_e - \alpha v$. Since $\nu_0^{0,0}$ is known, we can find the B_e 's. If we tentatively assume reasonable values for the α 's, then the B_1 's and B_2 's may be predicted. With the assumption of linear variation of the *B*'s with the *v*'s, it follows from a study of observed second differences in the series constituting the bands (0,0), (1,1), (2,2), that α' and α'' are very nearly equal.

The points in the (1,1) and (2,2) series of band lines at which the first differences equal four times the predicted B_1'' and B_2'' are then the predicted positions for $\nu_0^{1,1}$ and $\nu_0^{2,2}$, respectively. Assuming α'' to be in the neighborhood of 0.02 cm^{-1} , which is an average of the observed

α 's for other states of C_2 ($d^1\Pi_g$, 0.0255; $B^3\Pi_g$, 0.0173; $b^1\Pi_u$, 0.0174; $A^3\Pi_u$, 0.0149), the only possible choice of ν_0 's is that given in Table III.

These ν_0 's are found to give *B*'s and *D*'s that vary linearly with *v*, with $\alpha' = 0.204 \text{ cm}^{-1}$, $\alpha'' = 0.195 \text{ cm}^{-1}$. Now considering other choices for the ν_0 's, the smallest shifts that one can make from the above choice for $\nu_0^{1,1}$, namely, distances $+4B_1$ or $-4B_1$, give $\alpha \approx 0.04$ and 0.00 cm^{-1} , respectively. Either value appears unreasonable, and any other choice of $\nu_0^{1,1}$ is worse. Furthermore, any assumed shift in the positions of the several ν_0 's must be of the form $\pm 4B_v v$ to preserve the linearity of the *B*'s and *D*'s with *v*. This indicates a minimum shift of $\pm 8B_2$ and $\pm 12B_3$, or two and three full line intervals, respectively, in the (2,2) and (3,3) bands. Such large shifts seem also to be excluded in the case of the (3,3) band on the basis of intensities (cf. Fig. 3).

The next step in the analysis is the evaluation of the molecular constants, making use of the

TABLE II. $\Delta_2 F_v(J)$ values.

$\Delta_2 F''(J)$				$\Delta_2 F'(J)$			
<i>J</i>	$v'=0$	$v'=1$	$v'=2$	<i>J</i>	$v'=0$	$v'=1$	$v'=2$
1	11.1	12.0	11.3	2	18.5	18.0	18.0
3	25.5	26.0	24.7	4	32.9	33.0	31.7
5	39.9	39.6	39.0	6	47.5	46.8	46.1
7	54.4	53.5*	53.8	8	61.8	60.7*	61.5
9	68.7	67.8	68.2	10	76.5	75.9	75.9
11	83.2	82.8	82.3	12	91.0	90.6	89.6
13	97.5	96.9	95.9	14	105.6	104.4	103.2
15	112.2	110.8	109.3	16	120.2	118.5	117.2
17	126.7	125.2*	123.3	18	134.6	133.0*	131.3*
19	140.8	139.4	138.1*	20	148.9	147.4	146.0*
21	155.2	153.7	152.6	22	163.5	161.8	160.4
23	169.6	167.9	165.8	24	177.9	175.8	173.7
25	183.8	181.9*	179.8	26	192.2	190.3*	187.7
27	198.0*	196.1*	193.9	28	206.2*	204.2*	202.2*
29	212.2*	210.2*	208.2*	30	220.7*	218.6*	216.3*
31	226.5*	224.5*	222.0	32	235.0*	232.7*	230.1
33	240.4*	238.2*	235.5	34	249.2*	246.7*	243.8
35	254.7*	252.3	250.8*	36	263.1*	260.7	258.9*
37	268.5*	265.9	263.7	38	277.3*	274.3	271.9
39	282.5	279.7*	277.6	40	291.2	288.4*	285.7
41	296.6	294.0*		42	305.3	302.3*	
43	310.4	307.8*		44	319.5	316.1*	
45	324.4	321.3*		46	333.1	329.9*	
47	338.3			48	347.1		
49	351.8*			50	360.8*		
51	365.4			52	374.2		
53	379.1			54	388.0		
55	392.4*			56	401.2		
57	405.5*			58	414.6*		
59	418.8						

* This symbol is to indicate differences between lines which are neither blended nor very weak. All the rest may be less accurate.

usual combination differences

$$\Delta_2 F_v'(J) \equiv F_v'(J+1) - F_v'(J-1) = R(J) - P(J), \quad (1)$$

$$\Delta_2 F_v''(J) \equiv F_v''(J+1) - F_v''(J-1) = R(J-1) - P(J+1). \quad (2)$$

The $\Delta_2 F_v(J)$ values for the $\lambda 2300$ bands are given in Table II, assuming J assignments as in Fig. 3, which is based on the preceding discussion.

Assuming the usual expression

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots, \quad (3)$$

we have

$$\Delta_2 F_v(J)/(J+\frac{1}{2}) = 4B_v - 8D_v(J+\frac{1}{2})^2 + \dots \quad (4)$$

If the expression on the left is plotted against $(J+\frac{1}{2})^2$, the graph should be a straight line, provided powers of $(J+\frac{1}{2})$ higher than the second are negligible in Eq. (4), as proved to be the case here. We can determine B_v and D_v , respectively, from the $J=0$ intercept and the slope of the graph.

A related method consists in plotting the left side of the equation

$$4B_v(J+\frac{1}{2}) - \Delta_2 F_v(J) = 8D_v(J+\frac{1}{2})^3 \quad (5)$$

against J .⁹ Using this method (cf. reference for details) the previously obtained B values were checked, and slightly different D values than before were obtained. These D 's were averaged with those obtained by the first graphical method.

The best values for the ν_0 's were obtained by use of the formula

$$\nu_M = \nu_0 + (B' + B'')M + (B' - B'' + D' - D'')M^2 + 2(D' + D'')M^3 + (D' - D'')M^4 \dots, \quad (6)$$

where M is the well-known serial number. After substituting the known B 's and D 's for a given band the ν_M 's of its unblended lines were introduced and the equation solved for ν_0 . The values so obtained were averaged for each band to give the final ν_0 's. The B and D values obtained above and the ν_0 's are collected in Table III together with estimates of their reliability.

The analysis assumes that the bands conform to case a of Fig. 2. This is probably correct, but,

as discussed in the text, case b cannot be excluded with certainty. Case b would give slightly lower ν_0 's and B 's. Using

$$B_v = B_e - \alpha(v + \frac{1}{2}), \quad (7)$$

and

$$D_v = D_e - \beta(v + \frac{1}{2})$$

in connection with Table III, we find values of α , β , B_e , and D_e for the upper and lower $^1\Sigma^+$ states. These are collected in Table IV. From the B_e 's the internuclear distances r_e are also calculated in the usual manner. The ω_e 's have also been determined approximately from the well-known relation $\omega_e = (4B_e^3/D_e)^{1/2}$, and are given in Table IV.

It will be noticed that the ω_e values just calculated using $\omega_e = (4B_e^3/D_e)^{1/2}$ obey the relation $\omega_e' > \omega_e''$, which is the usual relation when $B_e' > B_e''$, as is true here. Definite evidence will now be produced, however, showing that actually $\omega_e'' > \omega_e'$, so that the relation $\omega_e' > \omega_e''$ just obtained must be attributed to small errors in the D_e 's (about ± 2 percent).

From the formulas for the positions of the ν_0 's of the bands in a sequence, it is readily shown that, very nearly, the distance between zeros of two successive bands is

$$\nu_0^{v', v''} - \nu_0^{v'-1, v''-1} = (\omega_e' - \omega_e'') - 2v'(\omega_e'x_e' - \omega_e''x_e''). \quad (8)$$

Now from Table III, $\nu_0^{1,1} - \nu_0^{0,0}$ is -25.84 cm^{-1} and $\nu_0^{2,2} - \nu_0^{1,1}$ is -25.62 cm^{-1} . Using Eq. (8), we then find $\omega_e' - \omega_e'' = -26.06 \text{ cm}^{-1}$, and $\omega_e'x_e' - \omega_e''x_e'' = -0.11 \text{ cm}^{-1}$. We note that the accurate value of $\omega_e' - \omega_e''$ thus obtained is opposite in sign to the rough value that was calculated above. The best way to combine the approximate values of ω_e' and ω_e'' obtained above

TABLE III. Rotational constants and ν_0 's from analysis of $\lambda 2300$ band, all in cm^{-1} . The estimated probable errors in order of increasing v are: For ν_0 's, ± 0.02 , ± 0.03 , ± 0.05 , and $\pm 0.20 \text{ cm}^{-1}$; B 's, ± 0.0002 , ± 0.0005 , ± 0.0005 , and $\pm 0.005 \text{ cm}^{-1}$; D 's, ± 0.05 , ± 0.1 , $\pm 0.2 \times 10^{-6} \text{ cm}^{-1}$.

BAND	ν_0	B'	B''	$D' \times 10^6$	$D'' \times 10^6$
0-0	43,227.23	1.8232	1.8125	7.54	7.39
1-1	43,201.39	1.8026	1.7927	6.87	6.47
2-2	43,175.77	1.7825	1.7735	6.15	5.50
*3-3	43,150.56	1.762	1.754		

⁹ Cf. G. Herzberg, *Molekülspektren und Molekülstruktur* (Leipzig: Steinkopff, 1939), pp. 139-142.

* The range of measured and unblended lines in the (3,3) band is so restricted that accurate ν_0 's and B 's could not be had. $\nu_0^{3,3}$ by extrapolation from the values of the other ν_0 's is $43,150.27 \text{ cm}^{-1}$.

TABLE IV. Constants from analysis of $\lambda 2300$ band (cm^{-1}).

	B_e	D_e	α	β	ω_e	ω_e^*	$r_e(\text{\AA})$
Upper $^1\Sigma$	1.8334	7.89×10^{-6}	0.0204	7.0×10^{-7}	1767	1748	1.2382
Lower $^1\Sigma$	1.8223	7.86×10^{-6}	0.0195	9.4×10^{-7}	1755	1774	1.2419

* The ω_e^* values are the best that could be had. See discussion in text.

with the accurate $\omega_e' - \omega_e''$ is to average the former and then add and subtract 13 cm^{-1} , so as to make $\omega_e' - \omega_e''$ correct. The results are $\omega_e' = 1748 \text{ cm}^{-1}$ and $\omega_e'' = 1774 \text{ cm}^{-1}$ (the quantities ω_e^* of Table IV).

There is an approximate relation given by Mecke and Birge which states that for all electronic states of a given diatomic molecule $B_e/\omega_e = \text{constant}$. It is found that for previously reported states of C_2^{10} this ratio varies from 0.98×10^{-3} to 1.01×10^{-3} . In the present case these ratios become $B_e'/\omega_e' = 1.04 \times 10^{-3}$ and $B_e''/\omega_e'' = 1.027 \times 10^{-3}$. The results are, therefore, in satisfactory agreement with the others.

It is interesting to calculate roughly where the $\Delta v = 1$ and $\Delta v = -1$ sequences of the present $^1\Sigma \rightarrow ^1\Sigma$ band system should occur. Substitution in the formulas for the ν_0 of electronic bands shows that⁷

$$\begin{aligned}\nu_0^{1,0} &= \nu_0^{0,0} + \omega_e' - 2x_e'\omega_e' + \dots, \\ \nu_0^{0,1} &= \nu_0^{0,0} - \omega_e'' + 2x_e''\omega_e'' - \dots.\end{aligned}\quad (9)$$

We have seen previously that $x_e'\omega_e' \approx x_e''\omega_e''$. We have also noted how various other coefficients for the $^1\Sigma \rightarrow ^1\Sigma$ transition are roughly equal to the

average of those for other states of C_2 . If then we assume $x_e'\omega_e' \approx x_e''\omega_e'' \approx 20 \text{ cm}^{-1}$, we shall probably not be in error by more than a few cm^{-1} . We then have $\nu_0^{1,0} \approx 44,956$ and $\nu_0^{0,1} \approx 41,473$. The (0,1) band ($B_0' - B_1'' = +0.0305 \text{ cm}^{-1}$) should degrade in the same direction as the (0,0) band ($B_0' - B_1'' = +0.0107$) but much more strongly. M_{head} is calculated to be about -59 . This corresponds to $\nu_{\text{head}} \approx 41,366$, a distance of 107 cm^{-1} from $\nu_0^{0,1}$. A band with head at $\nu = 41,284$ and degraded to the violet has been reported by Fox and Herzberg and may probably be interpreted as corresponding to the $\Delta v = -1$ sequence of the present system, as already suggested by Fox and Herzberg.³ The $\Delta v = +1$ sequence of bands is expected to be of the headless type ($B_1' - B_0'' = -0.0097$), as is the case in the $\Delta v = 0$ sequence, but with a tendency to degrade to the red. Fox and Herzberg report two bands, with heads at 45,061 and 45,100, which may perhaps belong to the $\Delta v = +1$ sequence of the present system, although they are reported to degrade to the violet contrary to our prediction.

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¹⁰ Cf. H. Sponer, *Molekülspektren*, Vol. I (Berlin: J. Springer, 1935), p. 14.

